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(21) International Application Number: PCT/US99/27819 (22) International Filing Date: 23 November 1999 (23.11.99) (30) Priority Data: 60/109,428 23 November 1998 (23.11.98) US (71) Applicant: MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037-0001 (US). (72) Inventor: GROSSER, Richard, W.; 6 Macclesfield Drive, Medford, NJ 08055 (US). (74) Agents: KEEN, Malcolm, D. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037-0001 (US).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: LIQUID UREA EXHAUST GAS TREATMENT ADDITIVE (57) Abstract Methods for the treatment of combustion effluent containing nitrogen oxides are provided. According to these methods, the combustion effluent is treated with a liquid treatment additive composition comprising urea, water and an oxygenated organic compound, in the presence of a catalyst. The treatment additive compositions of the present invention have lower freezing points than water/urea solutions, which allows use and storage of the treatment additive at temperatures below 10 °F (-12 °C), if necessary.		

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LIQUID UREA EXHAUST GAS TREATMENT ADDITIVE

This application relates to, and claims priority from, U.S. provisional patent application serial No. 60/109,428, filed on November 23, 1998.

5 U.S. Application Serial No. 09/ , filed concurrently (Mobil Case 10088-1), relates to a vehicle engine additive dispenser system.

The present invention is directed to a method for treating combustion effluent for removal of nitrogen oxides using liquid compositions of urea. Additives are present in the compositions to impart properties that make the compositions particularly useful
10 at low temperatures and in the treatment of motor vehicle exhausts.

The burning of hydrocarbon fuels in internal combustion engines results in the production and release of a mixture of combustion products. The major combustion products are carbon dioxide and water, both of which are usually accompanied by minor amounts of carbon monoxide (CO), nitrogen oxides (NO₂), and sulfur oxides
15 (SO₂). Oxides of nitrogen and sulfur have been implicated in the formation of smog, acid rain, and other atmospheric problems and are therefore considered to be undesirable pollutants. Various measures have been taken in the recent past to regulate the amount of these pollutants emitted from motor vehicles. While reduction of the amount of sulfur in fuels has led to lowered SO₂ emissions, the lowering of
20 nitrogen oxide content in vehicle emissions cannot be treated similarly. Advances in the design of engines as well as alterations in the composition of fuels may mitigate the production of nitrogen oxides; however, the combustion of air/fuel mixtures will always have the undesirable side effect of producing NO₂ emissions.

Due to the persistent problem of NO₂ emission from combustion processes,
25 the most effective strategy for reducing amounts of polluting nitrogen oxides involves the treatment of post-combustion emissions. To date, this strategy has been primarily applied to stationary industrial processes including furnaces, boilers, and stationary diesel engine applications. One method employed for the removal of NO₂ contaminants involves the treatment of combustion emissions with ammonia. In this
30 method, ammonia selectively reacts with NO₂ to give the innocuous reduction products of diatomic nitrogen (N₂) and water. When the reaction occurs by free radical formation and recombination at high temperatures, it has been termed selective non-catalytic reduction (SNCR). When the reaction occurs in the presence

of a catalyst, it is termed selective catalytic reduction (SCR). SCR-type processes for reducing NO₂ emissions have been favored over SNCR-type processes because of higher NO₂ removal efficiencies, lower ammonia consumption, and the production of fewer side products. However SCR treatments are more sensitive to the ratio of ammonia to NO₂. Thus, SCR has been adapted primarily for the treatment of NO₂-containing effluents of large scale, stationary, industrial processes which emit relatively constant quantities of NO₂. However recent advances in the precise dosing of liquid reagents has made possible the application of SCR to the treatment of effluents from devices, such as motor vehicles, with variable effluent compositions.

The ammonia used in an SCR process can also be generated in situ by thermal decomposition and hydrolysis of urea at high temperatures. Unlike ammonia, urea is a safe and tractable starting material, and can be used either as a solid or in solution. Several methods have been disclosed that utilize urea for the reduction of NO₂ emissions. U.S. Patent Nos. 4,208,386 and 4,325,924 describe the use of hydroxylic solutions of urea in the treatment of combustion effluent in noncatalytic treatment systems at sustained temperatures above 1300°F (705°C). U.S. Patent Nos. 4,719,092, 4,780,289, 4,978,514, 5,057,293, 5,286,467, and 5,298,230 reveal processes for the treatment of industrial combustion effluents using aqueous urea compositions containing additives which chemically enhance effectiveness. Despite the multitude of industrial applications for urea compositions in the treatment of NO₂ emissions, the above-mentioned urea compositions have not been designed for specifically maintaining liquidity at low temperatures so that they may remain useful under a wide range of climatic conditions. In addition, the known compositions are not directed for use in smaller, mobile applications, such as for the treatment of exhaust from motor vehicles.

Factors specific to mobile combustion engines must be considered in the design of potential exhaust treatment systems. First, the system must be composed of materials and components that are compact and light weight for maintaining efficiency and performance of the vehicle. Also, the system should be relatively easy to use, even by the unskilled user. In accordance, the materials of the system should also be capable of replenishment with a minimum amount of trouble and cost to the user as well as have safe-handling properties. In addition, the materials need to be easily manipulated, such as with a liquid, which can be readily stored, pumped, and

discharged on a moving vehicle. Furthermore, the materials should retain these desirable properties over a range of typical vehicle storage and operating temperatures.

Of particular importance for liquid exhaust treatments is the prevention of liquid phase changes at the low temperatures usually encountered by vehicle users in the colder climatic regions. Freezing is a particular problem of aqueous-based solutions thus creating a need for liquid exhaust treatments that will maintain the liquid state down to storage temperatures of -20°F (-30°C). In consideration of the potential application of SCR methods for the lowering of nitrogen oxide emissions in motor vehicle exhaust, specific urea formulations that will resist freezing at low temperatures are potentially important contributions to future reduction in air pollution.

The present invention relates to methods for treating combustion effluent containing nitrogen oxides. These methods involve treating the combustion effluent with a treatment additive in the presence of a catalyst. Preferable applications of the methods of the present invention are directed to the treatment of exhaust from motor vehicles, particularly those with diesel engines. The treatment additive comprises water and urea. A preferred treatment additive further comprises at least one oxygenated organic compound (or oxygen-containing organic compound) which is miscible with the aqueous urea solution. A preferred oxygenated organic compound is an alcohol. Applicant has discovered that the novel compositions of the present invention allow use and storage of the treatment additive at commonly encountered climatic conditions. Suitable alcohols include, but are not limited to, monohydric and polyhydric alcohols.

As used in this specification, the terms "fuel additive," "treatment agent" and "treatment additive" are used interchangeably and mean, collectively, a substance that is either added to fuel or employed to treat effluent derived from the combustion of fuel. A preferred "treatment additive" is an aqueous solution of urea and, optionally, an oxygenated organic compound (or oxygen-containing organic compound). An oxygenated organic compound includes an organic compound containing at least one oxygen atom. According to the present invention, an oxygenated organic compound includes, but is not limited to, alcohols, ethers, esters, aldehydes, ketones and carboxylic acids. Furthermore, an oxygenated organic compound may include any

substance having effective use in the treatment of gasoline and combustion processes.

As used in this specification, the term "combustion effluent" refers collectively to the products of the combustion of hydrocarbons in the presence of air which include carbon dioxide, water, hydrocarbons, carbon monoxide, sulfur oxides, and nitrogen oxides. The term "exhaust" is used to describe the combustion effluent emitted from motor vehicles. In addition, the term "reaction zone" refers to a device, means or location where combustion effluent and the urea composition are combined, the reaction zone usually containing one or more catalysts suitable for effecting hydrolysis of urea and SCR in a motor vehicle. A preferred reaction zone is an exhaust pipe of a motor vehicle. The exhaust pipe of a motor vehicle is a tube or pipe that connects the engine of the vehicle to the selective catalytic reduction (SCR) unit of the vehicle.

The term "nitrogen oxides" or "NO₂" refers collectively to both nitric oxide (NO) and nitrogen dioxide (NO₂). Hence, the term "NO₂ emissions" or "nitrogen oxide emissions" refers to NO₂ found in combustion effluent.

Alcohols are preferred oxygenated organic compounds. As used herein, the term "alcohol" means a chemical compound with at least one hydroxyl group that also possesses properties desirable for the present invention. "Alcohol" or "alcohols" include, but are not limited to, polyhydric alcohols (*i.e.*, compounds with more than one hydroxyl group, such as ethylene glycol, propylene glycol, glycerol, polyethylene glycol and polyoxyalcolamine glycol) and monohydric alcohols (*i.e.*, compounds with only one hydroxyl group, such as in methanol, ethanol, propanol, and isopropanol).

The present invention provides methods for treating combustion effluent containing nitrogen oxides (NO₂). In particular, the present invention relates to methods for reducing NO₂ emissions from combustion devices using a liquid treatment additive comprising urea, water and an oxygenated organic compound. A preferred oxygenated organic compound comprises an alcohol. Treatable combustion effluent may be derived from any mobile combustion device including, but not limited to, combustion engines including both spark-ignited and diesel. Specifically, the methods of the present invention are particularly suited for treatment of exhaust from combustion engines in motor vehicles including, but not limited to, cars, trucks, tractors, farm equipment, construction equipment, and the like. The methods of the

present invention preferably treat exhaust from motor vehicles operating with diesel engines which generally have higher NO₂ emissions.

According to the present invention, a liquid treatment additive comprising urea is combined with combustion effluent in a reaction zone before the effluent is released to the atmosphere. The treatment additive is stored in a storage container and may be added to the effluent by injection or spray. Preferably, the amount of treatment additive added is such that a maximum amount of NO₂ is reacted to form N₂ and water, and a minimum amount of byproducts, such as excess ammonia, are created. Preferably, the molar ratio of urea to NO₂ ranges from 0.1:1 to 1:1, or more preferably, is stoichiometric at 1:2. Elevated temperatures are also required in the reaction zone for both the decomposition of urea and the reaction of ammonia with NO₂. Effluent entering the reaction zone may range in temperature from ambient temperature to 1000°F (540°C). The reaction zone also contains one or more catalysts that can be of any known material or combination of materials used in the hydrolysis of urea or SCR reactions such as transition metals, or metal oxides. Specific catalysts (or SCR catalysts) include, but are not limited to, metal oxides, transition metal oxides, transition metals, precious metals, vanadium oxide, tungsten oxide, titanium oxide, iron oxide, manganese oxide, chromium oxide, copper oxide, zeolites, platinum, palladium, rhodium, and iridium. Catalyst materials are preferably mounted on supports composed of ceramics or zeolites.

In a preferred embodiment of the present invention, a treatment additive comprising urea is added to motor vehicle exhaust in a reaction zone prior to release of the exhaust to the atmosphere. Exhaust, requiring treatment, typically contains NO₂ in the range of 100 ppm to 1100 ppm. The treatment additive is added to the exhaust in amounts and molar ratios as described above. Prevailing temperatures in motor vehicle exhaust are sufficiently elevated to promote both the decomposition of urea to ammonia and the reaction of the resulting ammonia with NO₂ in the presence of any of the aforementioned catalysts or combination of catalysts. Exhaust temperatures in the reaction zone may range from ambient temperature to 1000°F(540°C). Treated exhaust has lowered NO₂ content which has been reduced by 30% to 99%, or more preferably, by 50% to 99%.

Preferred treatment additives according to the methods of the present invention include liquid compositions comprising water and urea. In a preferred

embodiment the treatment additive further comprises at least one oxygenated organic compound. In one embodiment the treatment additive comprises at least two oxygenated organic compounds. In other embodiments, the treatment additive comprises three or more oxygenated organic compounds. Preferred oxygenated organic compounds include alcohols. Alcohols according to the present invention include, but are not limited to, monohydric and polyhydric alcohols that are miscible with water and form aqueous solutions with a freezing point lower than that of water. Polyhydric alcohols are preferred. Examples of suitable polyhydric alcohols include, but are not limited to, ethylene glycol, propylene glycol, glycerol, polyethylene glycol, and polyoxyalcolamine glycol. A preferred polyhydric alcohol is ethylene glycol. Monohydric alcohols are also amenable to the methods of the present invention. Monohydric alcohols which may be suitable according to the methods of the present invention include, but are not limited to, methanol, ethanol, propanol, and isopropanol.

The treatment additive may further comprise other agents including, but not limited to, demineralizers and dyes. Demineralizers may be added to prevent scaling, which would decrease the efficiency of the methods of the claimed invention. Dyes may also be added to the treatment additive or to potentially toxic components such as the alcohol of the treatment additive to ensure safe handling.

The amounts of each component in the treatment additive compositions are determined by the intended application of the present invention. Generally, however, it is favorable to maximize the relative amount of urea in the composition so that a minimal volume of treatment additive may be used to effectively treat nitrogen oxide-containing effluents. Similarly, it is desirable to include an oxygenated organic compound in an amount that is sufficient to obtain a target freezing point. Target freezing points of the liquid compositions preferably lie below the freezing point of a urea/water solution (for example, 10°F or -13°C for a 30% urea solution by weight), although below -15°F (-26°C) is more preferable, and at or lower than -20°F (-29°C) is even more preferable. Furthermore, it is desirable to include water in the composition in an amount that is sufficient to maintain urea in solution. In a preferred embodiment, the treatment additive composition comprises 30% to 70% by weight of water, 20% to 40% by weight of urea, and 1% to 40% by weight of an oxygenated organic compound. More preferable treatment additive compositions comprise 35% to 45% by weight of water, 25% to 35% by weight of urea, and 25% to 35% by

weight of an oxygenated organic compound. In another preferred embodiment, the treatment additive composition comprises 40% by weight of water, 30% by weight of urea, and 30% by weight of an oxygenated organic compound. A preferred oxygenated organic compound is ethylene glycol.

5 The treatment additive compositions of the present invention can be stored and used over a wide range of temperatures. These compositions store particularly well at low temperatures because they possess lower freezing points than water/urea solutions, enabling them to remain in the liquid state when temperatures may regularly or occasionally fall below the freezing point of a urea/water solution (for example, 10°F or -13°C for a 30% urea solution by weight). Because of this property, the treatment
10 additive compositions of the present invention are particularly useful in applications where combustion devices operate in temperatures below 10°F (-13°C).

EXAMPLES

15 Example 1

A urea blend suitable for use in the treatment of vehicle exhaust

An aqueous solution containing 40% water by weight, 30% urea by weight, and 30% ethylene glycol by weight was formulated. The freezing point of the solution was determined to be -20°F (-29°C) at which point the liquid turned to slush.

20 Example 2

A urea blend suitable for use in the treatment of vehicle exhaust

An aqueous solution containing 50% water by weight, 30% urea by weight, and 20% ethylene glycol by weight was formulated. The blend remained clear and
25 fluid at -15°F (-26°C).

Example 3

Treatment of exhaust from a diesel vehicle with a liquid urea composition

Exhaust evolving from a motor vehicle diesel engine contains 4 g/mile average
30 amount of NO₂ and has an average temperature of 400°F. An amount of 13 g/mile of solution containing 40% water by weight, 30% urea by weight, and 30% ethylene glycol by weight is added to the exhaust by a spray means. The exhaust and spray mixture is passed over a zeolite catalyst where NO₂ is reacted. Treated exhaust exits

the vehicle with an NO₂ content of 0.4 g/mile (0.25 g. km.⁻¹) showing an overall reduction of 3.6 g/mile (2.2 g. km.⁻¹) of NO₂ in exhaust emissions, which is similar to exhaust treated with an aqueous urea solution lacking an oxygenated organic compound.

CLAIMS:

1. A method of treating exhaust from a motor vehicle, the exhaust containing nitrogen oxides, the method comprising adding a treatment additive comprising water and urea to the exhaust.
5
2. The method of claim 1 in which the treatment additive further comprises at least one oxygenated organic compound.
- 10 3. The method of claim 1 in which the motor vehicle is operated with a diesel engine.
4. The method of claim 1 further comprising adding the treatment additive to the exhaust in the presence of an SCR catalyst.
- 15 5. The method of claim 2 in which the oxygenated organic compound is an alcohol.
6. The method of claim 5 in which the alcohol is ethylene glycol, propylene glycol, polyethylene glycol, glycerol or polyoxyalcolamine glycol.
20
7. The method of claim 5 in which the alcohol is methanol, ethanol, propanol or isopropanol.
- 25 8. The method of claim 2 in which the treatment additive comprises 30% to 70% by weight of water, 20% to 40% by weight of urea, and 1% to 40% by weight of oxygenated organic compound.
9. The method of claim 8 in which the treatment additive comprises 35%
30 to 45% by weight of water, 25% to 35% by weight of urea, and 25% to 35% by weight of ethylene glycol.

10. The method of claim 15 in which the treatment additive comprises 40% by weight of water, 30% by weight of urea, and 30% by weight of ethylene glycol.

5 11. A diesel engine exhaust treatment additive comprising 30% to 70% by weight of water, 20% to 40% by weight of urea, and 1% to 40% by weight of oxygenated organic compound.

10 12. The treatment additive of claim 11 comprising 35% to 45% by weight of water, 25% to 35% by weight of urea, and 25% to 35% by weight of oxygenated organic compound.

13. The treatment additive of claim 12 comprising 40% by weight of water, 30% by weight of urea, and 30% by weight of oxygenated organic compound.

15 14. The treatment additive of claim 23 in which the oxygenated organic compound is ethylene glycol.

20 15. The treatment additive of claim 11 in which the alcohol is ethylene glycol, propylene glycol, polyethylene glycol, glycerol or polyoxyalcolamine glycol.

16. The treatment additive of claim 11 in which the alcohol is methanol, ethanol, propanol or isopropanol

INTERNATIONAL SEARCH REPORT

International application No.

P 599/27819

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B01D 47/00, 53/34; B01J 8/00; C01B 21/00

US CL : 423/212, 235

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/212, 235; 252/189

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	US 5,976,475 A (PETER-HOBLYN et al) 02 November 1999, col. 3, line 44 - col. 4, line 49.	1-5, 7-13, 16
Y	US 4,780,289 A (EPPERLY et al) 25 October 1988, col. 8, lines 42-46.	6, 9, 14, 15
A	US 4,626,417 A (YOUNG) 02 December 1986, see entire document.	

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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